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On Dielectric Relaxation due to Oxycarbonyl Groups Present in Cellulose Triacylates

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Abstract—From the results of the dielectric relaxation experiment for 2,3-di-O-acetyl-6-O-trityl cellulose, the dielectric β_d process observed for a series of cellulose triacylates in the glassy state was found to arise from the orientational polarization of the oxycarbonyl groups which are introduced not only at C-6 position but also at C-2 and C-3 positions of a glucopyranose ring.

Introduction

In the glassy state, cellulose exhibits a dielectric relaxation process which is assigned to the orientational polarization of the hydroxyl groups in amorphous region. However, only the hydroxyl groups attached to C-6 position are known to cause the process, since they can rotate around C-5 and C-6 axis¹⁾. On the other hand, cellulose triacylates from the acetate to stearate exhibit a dielectric process in the glassy state, which is labelled β_d ²⁾. This process was concluded to be due to the orientational polarization of the oxycarbonyl groups in the acyl side chain. In relation to the dielectric process of cellulose mentioned above, it is most probable that the β_d process of the triacylates is stemmed from the orientational polarization of the oxycarbonyl groups at C-6 position. Therefore, it is important to clarify whether or not the oxycarbonyl groups attached to C-2 and C-3 positions are responsible for the β_d process of the triacylates. For this purpose, we investigated the dielectric properties of 2,3-di-O-acetyl-6-O-trityl celluloses (ATC) whose C-6 position is completely blocked by a dielectrically non-active trityl group.

Experimental

According to the procedure reported by Hagiwara *et al.*²⁾, we prepared trityl cellulose with D.S. of ca. 1.0, in which almost all the hydroxyl groups at C-6 position of a gluco-pyranose ring are blocked by the trityl groups. To a solution of this trityl cellulose (1 g) dissolved in pyridine (12.5 ml) was added acetyl anhydride (10 ml). After the solution was kept at 90°C for 9 hrs with stirring, it was poured into an excess

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of methanol to precipitate ATC. The dielectric measurements of thus obtained ATC were made in the temperature range from 20 to -60°C and over the frequency from 50 Hz to 1 MHz.

Results and discussion

From the dielectric loss versus temperature curves for ATC at respective frequencies, a process was recognized in similar temperature and frequency ranges to the β_d process for the triacylates, though the maximum loss value was substantially small as compared to that for the triacylates. This process for ATC seems to reflect the orientational polarization of the oxycarbonyl groups in the acyl side chain as in the case of the triacylates, since trityl cellulose exhibits no relaxation process in the corresponding temperature and frequency ranges³⁾. In order to obtain further information, the logarithmic frequency was plotted against the reciprocal of the absolute temperature at loss maximum for the process of ATC. The results are shown in Figure 1.

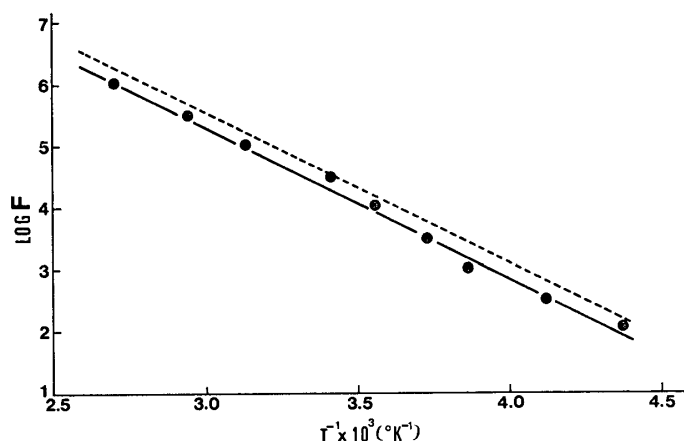


Figure 1 Plots of logarithmic frequency (F) against the reciprocal of the absolute temperature (T^{-1}) at dielectric loss maximum for the process of 2,3-di-O-acetyl-6-O-trityl cellulose. The dashed line indicates the results for the β_d process of cellulose triacylates²⁾.

Obviously, they are related linearly. The regression line obtained is parallel to the dashed line which is the results for the β_d process of cellulose acylates from the acetate to stearate²⁾. The values of apparent activation energy of the processes for ATC and the triacylates were 11.3 and 11.4 kcal/mol, respectively, indicating that both the processes result from a common origin. Hence, the process for ATC can be attributed to the orientational polarization of the oxycarbonyl groups attached to C-2 and C-3 positions of a gluco-pyranose ring. From these findings, the β_d process for cellulose triacylates is considered to be due to the oxycarbonyl groups not only at C-6 position but also at C-2 and C-3 positions.

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